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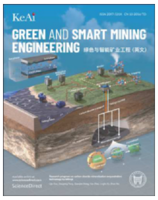

Ecofriendly leaching agents for copper extraction—An overview of amino and organic acid applications

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ABSTRACT

The green transition's push for electrification has substantially increased the demand for copper, making it a critical raw material. This extravagant demand has made it profitable to extract copper from low-grade sulfide ores, which contain less than 0.3wt% copper. However, processing such low-grade ores requires extensive amounts of chemicals, raising environmental concerns. Thus, several investigations have been conducted on non-traditional lixiviants for copper extraction. Surprisingly, few studies have comprehensively reviewed this area to provide a comprehensive understanding and highlight gaps. This review analyzes investigations that have worked on the leaching process of copper into solutions using environmentally friendly reagents, particularly organic acids and amino acids, and compare them to conventional inorganic acids and examines recent advancements in ecofriendly leaching agents, specifically their application in copper leaching. The primary objective is to highlight the significance of these green reagents in mobilizing copper from solid to solution phases. It was highlighted that factors, such as mineralogy, mechanical activation, impurities, particle size, temperature, and initial concentration of the leaching agent, influence the leaching efficiency of organic and amino acids from primary and secondary copper resources. These variables interact in more complex ways than those encountered with conventional leaching methods. Research in this area has shown promising results, both in terms of extraction efficiency and reduced environmental impact, making it an exciting and essential area for further exploration and development. This shift towards using nonconventional lixiviants represents a significant step forward in the quest for more sustainable and environmentally responsible mining practices and recycling processes.

1. Introduction

Copper is a highly sought-after metal worldwide, with a staggering demand of 22 million tons annually [1]. Its adaptability is showcased across various industries, from electronics manufacturing and power grids to transportation and construction. Copper is known for its malleability and flexibility (Fig. 1), as well as for its excellent corrosion resistance and superior conductivity for electricity and heat [2]. Most global copper reserves exist in sulfide minerals (chalcopyrite, bornite, covellite, chalcocite, etc.), with only a small portion comprising oxides [3]. Traditional copper extraction typically involves leaching with sulfuric acid (H_2SO_4) as a lixiviant. Copper oxides dissolve easily in a diluted sulfuric acid solution, but primary refractory sulfides necessitate high temperatures and pressures, and secondary sulfides require additional oxidants [4] for effective dissolution. Addressing the challenges of declining ore reserves and grades, environmental concerns, and the challenges associated with sulfuric acid usage, researchers are exploring alternative processes for treating low-grade sulfide ores. These alternatives could offer potential solutions to high operational and capital costs [5]. Chalcopyrite, the most abundant copper sulfide mineral, comprising about 70% of copper's resources, has a very low dissolution rate using sulfuric acid owing to the formation of a passivation layer on its surface [6,7]. By contrast, copper oxide minerals face issues such as excessive carbonate consumption, conversion of silicates into gel-like substances, and dissolution of iron impurities, which can hinder effective leaching by sulfuric acid [8].

In recent years, the quest for sustainable and environmentally friendly methods for copper leaching has led to the exploration of

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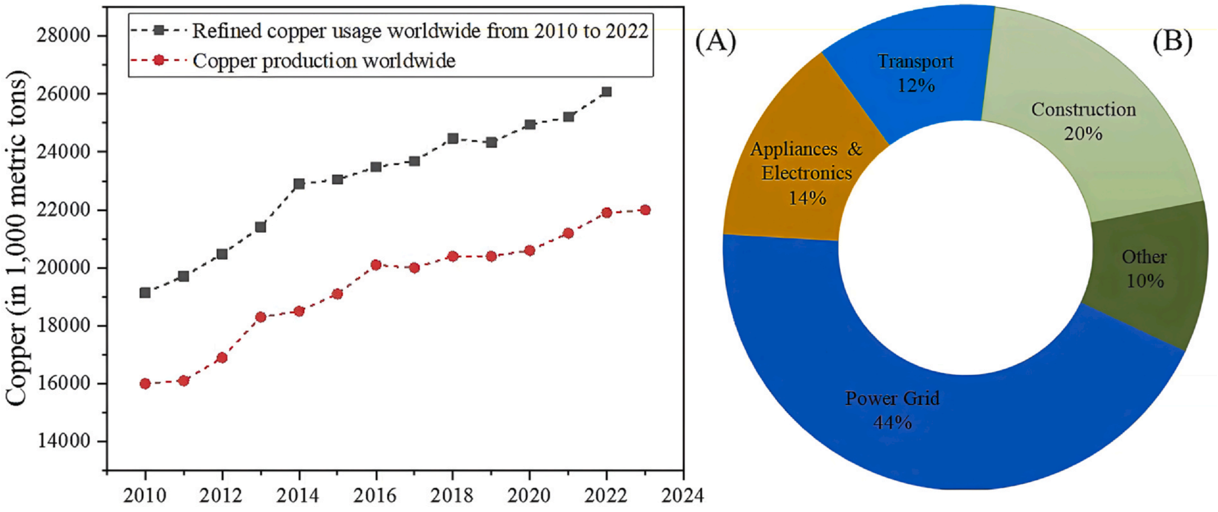

Fig. 1. (A) Refined copper usage and production worldwide from 2010 to 2022 [9]. (B) Major end uses of copper worldwide in 2023 [10].

alternatives to sulfuric acid [11]. This green transition has highlighted the potential of employing amino acids and organic acids as effective solvents. Amino acids, in particular, have been proven to be an effective and environmentally friendly group of leaching reagents, indicating an important role in copper recovery [12,13].

Glycine stands out among amino acids for copper leaching thanks to its low cost, simple structure, high metal affinity, and industrial availability [14–16]. Glutamic acid is also gaining attention for its nontoxic nature and cost-effectiveness in copper dissolution [17–19]. These organic acids offer several advantages, such as biodegradability, lower secondary pollution, high metal selectivity, and recyclability. They are used to leach metals from low-grade ores and can contribute hydrogen ions to form metal complexes, acting as potent leaching agents [20].

Several different leaching agents have been used for copper extraction, with some review articles documenting their use in general copper leaching [16,21,22]. Li *et al.* (2022) [13] presented a review of articles that use glycine for metal dissolution in ores, concentrates, and waste compared to the traditional system using cyanide. The study revealed that glycine can dissolve most copper oxide and sulfide minerals, as well as native copper. However, more aspects of this field have been comprehended recently.

This review aims to comprehensively summarize existing research on green leaching agents for copper extraction, focusing on amino and organic acids. It also seeks to identify contradictions in previous studies, analyze reaction mechanisms, and highlight areas needing further exploration.

2. Amino acids

Amino acids are organic compounds characterized by an amine group, a carboxylic group, and a sidechain specific to each type. Recently, they have gained attention in extractive metallurgy as a “green” lixiviant for copper recovery.

2.1. Glycine

Glycine, the simplest amino acid with the chemical structure NH_2CH_2COOH (Fig. 2), has been widely used in various industries such as medicine and mineral processing. Glycine is nontoxic, nonvolatile, sweet-tasting, nonflammable, colorless, crystalline solid, and eco-friendly [23,24].

Glycine, in specific bacterial environments, can enhance cyanide production. Cyanogenic bacteria can increase cyanide levels [26,27], while other bacteria, such as cell suspensions of *Proteus* and *Pseudomonas aeruginosa*, can oxidize glycine into ammonia, carbon dioxide, water, and cyanide [28]. Glycine has low consumption and is economically produced (Free on Board (FOB) 1500–2000 USD/t) on an industrial scale [8,29].

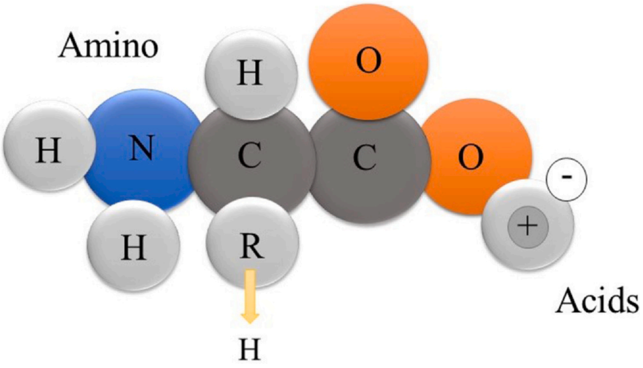

Fig. 2. Schematic structure of amino acids and glycine [25].

Notably, glycine can dissolve various metals, including copper, gold, silver, arsenic, vanadium, and cobalt, by forming complexes, making it a promising alternative to traditional sulfuric acid leaching methods [30–33]. Glycine can be used effectively in copper resources with various impurities and carbonate ores [34]. Based on the following reactions, glycine could be complex with cupric and cuprous ions Eqs. (1)–(3) [35].

$$Cu^{2+} + H_2NCH_2COO^- \rightarrow Cu(H_2NCH_2COO)^+, \lg K = 8.6 \quad (1)$$

$$Cu^{2+} + 2H_2NCH_2COO^- \rightarrow Cu(H_2NCH_2COO)_2, \lg K = 15.6 \quad (2)$$

$$Cu^+ + 2H_2NCH_2COO^- \rightarrow Cu(H_2NCH_2COO)_2^-, \lg K = 10.1 \quad (3)$$

Recent studies have focused on using alkaline glycine solutions as a lixiviant for the leaching and recovery of copper ores. This research shows that various copper minerals dissolve effectively in these solutions. In an alkaline solution, dissolved copper is stabilized by anionic glycine to form either Cu(I)–glycine or Cu(II)–glycine [36].

For copper oxides, recovery rates (Table 1) of 83%–95% have been documented for minerals like azurite, malachite, and cuprite [8], with complete copper recovery from cuprite [32]. However, the dissolution rate for cuprite can vary across studies [37]. Hydrogen peroxide (H_2O_2) is typically used as the main oxidant, with most experiments conducted at room temperature and a pH of about 11, except for some studies on chalcopyrite. Copper oxide minerals mostly dissolve within 24 h, while secondary and primary sulfides such as covellite and chalcopyrite may require up to 96 h for maximum dissolution at room temperature.

Table 1
Dissolution of the different copper minerals in the glycine medium.

Classification	Minerals	Formula	Oxidant	[Gly]	T (°C)	Time (h)	pH	Pyrite content (wt%)	Cu dissolution (%)	Ref.
Oxides	Azurite	$2CuCO_3Cu(OH)_2$	—	Gly:Cu 4:1	RT	24	11	Not reported	95	[8]
	Malachite	$CuCO_3Cu(OH)_2$	—	Gly:Cu 4:1	RT	24	11	Not reported	91	[8]
	Cuprite	Cu_2O	—	Gly:Cu 4:1	RT	24	11	Not reported	83.8	[8]
			3% H_2O_2	Gly:Cu 4.9:1				1–2	52	[38]
			1% H_2O_2	0.3 M	RT	48	11	28.55	100	[32]
	Chrysocolla	$CuSiO_3{\cdot}2H_2O$	—	Gly:Cu 4:1	RT	24	11	Not reported	17.4	[8]
	Conichalcite	$CaCuAsO_4OH$	3% H_2O_2	0.5 M	RT	24	> 11	3	12.1	[39]
	Native Copper	Cu	1% H_2O_2	0.3 M	RT	48	11	28.55	100	[32]
			3% H_2O_2	Gly:Cu 4.9:1				1–2	52	[38]
Secondary sulfides	Chalcocite	Cu_2S	8 ppm O_2	0.5 M	RT	24	11	Not reported	40	[40]
			1% H_2O_2	0.3 M	RT	48	11	28.55	100	[32]
	Covellite	CuS	1% H_2O_2	0.3 M	RT	48	11	28.55	19	[32]
Primary sulfides	Chalcopyrite	$CuFeS_2$	1% H_2O_2	0.3 M	RT	48	11	28.55	80	[32]
			25 ppm O_2	0.2 M	RT	24	11.5	Not reported	19	[36]
			3% H_2O_2	1 M	RT	96	11	5	21	[41]
			3% H_2O_2	0.5 M	RT	96	> 11	3	20.7	[39]
			15 ppm O_2	0.5 M	60	96	11.5	10	39	[42]
			1 L/min O_2	0.7 M	60	6	10.5	9	41	[43]
			25 ppm O_2	0.2 M	60	24	11.5	Not reported	36	[36]
			1 L/min O_2	0.4 M	60	24	10.5	0	19	[44]
	Bornite	Cu_5FeS_4	1% H_2O_2	0.3 M	RT	48	11	28.55	92	[32]

Notes: RT: Room temperature. *T*: Temperature.

Chalcopyrite, chrysocolla, and conichalcite are three highly refractory copper ore minerals [30,38,39]. It was observed that 80% of chalcopyrite, 100% of chalcocite, and metallic copper can be dissolved by glycine from a gravity gold-copper concentrate. It should be noted that copper dissolution from chalcopyrite by glycine is normally as low as 20%, however, it can be largely enhanced by the high ore's pyrite content [36,39,41]. The mineral composition and the ratio between copper sulfide minerals and pyrite (galvanic interactions) significantly affect copper recovery [36,38–40].

2.1.1. Leaching of copper sulfide minerals by glycine

Eksteen *et al.* (2017) [36] introduced a conceptual process for extracting copper from chalcopyrite using a glycine solution. They observed that increasing certain process parameters, such as temperature (up to 60 °C), glycine concentration, pH (9.2–11), and dissolved oxygen concentration, significantly enhances the rate of copper dissolution. Notably, reducing particle size to below 10 µm dramatically boosted the rate of copper dissolution from 40.1% to 92.0% at 60 °C. Particle size reduction liberates more chalcopyrite, increases the surface area, and leads to higher copper recovery. However, when temperatures exceed 60 °C, copper extraction decreases owing to glycine's conversion to glycinate and decreased oxygen concentration in the solution. Additionally, pH levels above 10.5 result in decreased copper recovery owing to copper sulfide precipitation. This emphasizes the importance of mineralogy in determining the proper process pH, as many studies have conducted experiments at a pH of around 11 or higher (Table 1). Furthermore, increasing solid content decreases copper dissolution owing to higher copper concentration in the solution, leading to potential copper precipitation [43].

Mechanical activation also shows promise for glycine leaching; treating chalcopyrite with a planetary mill for 4 h (resulting in a fraction size less than 20 µm) and then mechanically activating it for 12 h at 60 °C resulted in 95.1% copper dissolution. This indicates that mechanical activation could be a promising method for enhancing copper extraction prior to glycine leaching, even for low-grade chalcopyrite concentrations [44]. Overall, these findings highlight the importance of optimizing factors such as temperature, pH, solid content, and mechanical activation in copper extraction using glycine solution.

2.1.2. Leaching of copper oxide minerals by glycine

Conventional methods of leaching copper oxide minerals involve using acids, particularly sulfuric acid. However, these can lead to several challenges, including gel formation, impurities in the dissolution process, high leaching agent consumption, difficulties in dissolving high calcium–magnesium carbonate, and environmental hazards [45]. Selective copper lixiviants, such as ammonia, have been examined to address these issues, showing promise as a selective copper-leaching agent [22]. Still, ammonia presents challenges like toxicity, adverse effects on skin and eyes [46], and difficulties in recycling and reusing [47]. An alternative lixiviant, glycine, has been identified as a selective copper reagent that overcomes the challenges associated with ammonia.

Tanda *et al.* (2017) [8] studied glycine leaching of various copper oxide minerals, including azurite, malachite, cuprite, and chrysocolla, achieving recovery rates of 95.0%, 91.0%, 83.8%, and 17.4% for each mineral, respectively, after 24 h at pH 11, with a molar glycine-to-copper ratio of 4:1. Notably, using the molar glycine-to-copper ratio to 8:1 led to the complete dissolution of copper from azurite in less than 6 h. The study also found that the rate of copper dissolution from azurite, malachite, and cuprite in the glycine solution was faster compared to that of chrysocolla.

2.1.3. Leaching of gold–copper minerals by glycine

The association of gold and copper in the concentrate poses several extraction challenges during gold recovery, including high cyanide consumption and negative effects on gold leaching.

During cyanide leaching, soluble copper forms toxic copper–cyanide complexes such as $Cu(CN)_2{}^-$, $Cu(CN)_3{}^{2-}$, and $Cu(CN)_4{}^{3-}$ [33]. The formation of copper cyanide complexes affects gold recovery in both the cyanide leaching process and the purification and refining stages. These effects mainly interfere with the gold cyanide reaction and carbon adsorption processes [48]. Thus, controlling the selective leaching of copper before cyanidation is crucial in the process. Traditionally, copper is removed from copper–gold ores using sulfuric acid before cyanide leaching, requiring an additional neutralization stage after copper leaching [49].

Glycine has emerged as an effective selective lixiviant for copper extraction from copper–gold concentrates, addressing these challenges. The glycine–cyanide synergy is particularly effective in ores containing copper and gold, significantly boosting gold dissolution rates, up to 6.5 times higher than traditional cyanide systems [50], while reducing cyanide consumption owing to copper's role as a cyanide consumer. Various studies propose a four-step gold dissolution process in the cyanide–copper–glycine system as follows [33,50]: (1) glycine dissolves gold as a parallel solvent, (2) glycine replaces cyanide in copper composition, (3) glycine facilitates the removal of CuCN and $Cu\ (OH)_2$ precipitates from the gold and copper surfaces, and (4) copper(II) glycine forms an additional oxidant, enhancing solubility and availability in the leach solution.

In this way, glycine forms complexes with both copper(I) and copper (II), preventing the formation of copper cyanide complexes. Glycine helps preserve cyanide availability, ensuring its effective use in dissolving gold, thereby enhancing the overall efficiency of the gold leaching process and potentially reducing cyanide consumption and its environmental impact. Furthermore, $Cu(OH)_2$ is an insoluble hydroxide that can form on the gold and copper surfaces. Glycine can chelate with Cu^{2+} ions, which helps in dissolving $Cu(OH)_2$ through the following reaction:

$$Cu(OH)_2 + 2Glycine \rightarrow Cu(Glycine)_2{}^{2+} + 2OH^- \quad (4)$$

This reaction converts the insoluble $Cu(OH)_2$ into a soluble complex, effectively cleaning the surface. This clean surface enhances the interaction between gold and the leaching solution, improving the dissolution rate of gold. Meanwhile, copper(II) ions serve as potent oxidizing agents, participating in redox reactions necessary for the leaching process. The presence of a soluble copper(II) glycine complex enhances the availability of Cu^{2+} ions in the solution, facilitating the oxidation of other species involved in gold dissolution.

Fig. 3 illustrates a schematic model of the glycine–cyanide synergistic system, showcasing its efficiency in optimizing the process.

Using glycine as a reagent in the copper leaching stage could eliminate the need for an additional neutralization step before gold leaching in cyanide solutions owing to its alkaline nature [15]. Studies have shown that when glycine is applied to a gold–copper concentrate, both with and without peroxide, significant copper extraction is achieved. At a pH of 10.5–11 and a glycine concentration of 0.3 M, approximately 100% of metallic copper, cuprite, and chalcocite, about 80% of chalcopyrite, and approximately 98% of the total available copper in the concentrate can be dissolved within 48 h under ambient conditions. Increasing glycine and peroxide concentrations led to higher copper extraction rates, although glycine alone is effective at dissolving copper. Adding 1% peroxide increases the total copper dissolution rate to 80%, while without peroxide, the rate is 75% [32]. Pyrite, a mineral that typically complicates traditional leaching processes of various valuable metals with typical leaching agents, remained intact by glycine owing to its selective nature. Furthermore, it should be noted that high copper extraction rates are linked to the presence of excessive amounts of pyrite and its respective galvanic interactions.

2.1.4. Kinetic studies of copper leaching by glycine

Kinetic studies on metal leaching using a glycine system mainly target copper leaching, exploring variables such as glycine concentration, dissolved oxygen, temperature, stirring speed, and particle size. The shrinking core model has been the main focus in these studies [40,42,51], revealing that copper extraction from minerals like malachite, azurite, and cuprite in aqueous alkaline glycine solutions is rapid. By contrast, copper extraction from chrysocolla seems to be poor and slow [30]. For copper sulfides such as chalcopyrite and chalcocite, the leaching process in a glycine medium is inherently slow under ambient conditions. However, the rate of copper leaching is considerably enhanced by applying ultrafine grinding, elevated temperatures, higher glycine concentrations, extensive oxygen supply, and periodic addition of oxidants [36].

(1) Effect of temperature.

According to studies, the initial copper dissolution rate from various minerals generally increases with rising temperatures [40,41]. Studies show that copper dissolution rate significantly increased as the temperature rose during malachite leaching in the alkaline glycine system. Maintaining a glycine concentration of 0.4 M, a particle size of 53–75 μm, and a stirring speed of 350 r/min, an increase in temperature from 25 to 50 °C enhanced the copper leaching rate but only during the first 5 min [51]. Although higher temperatures generally enhanced the copper dissolution rate, the increase became less pronounced after a 10 °C rise. It is well known that in chemical controlling processes, small

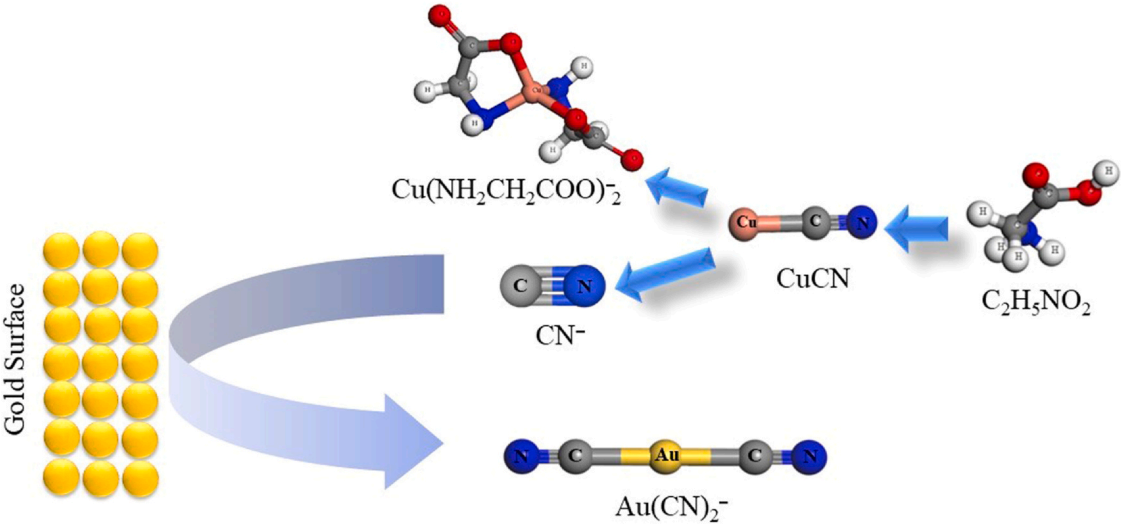

Fig. 3. Schematic modeling of the glycine–cyanide synergistic system efficiency in the gold–copper systems [33].

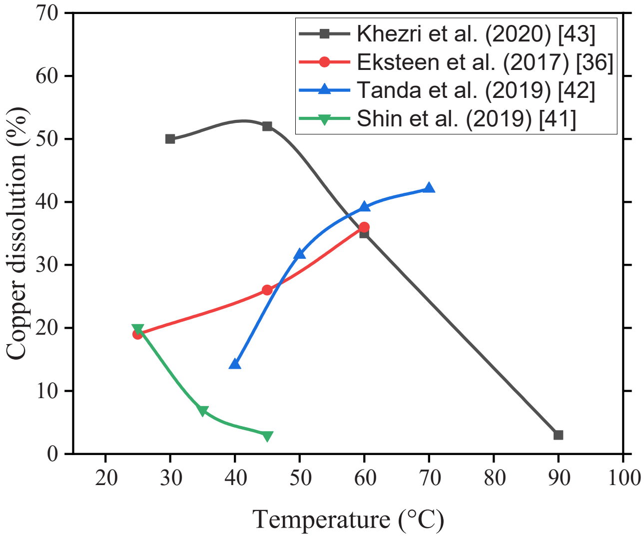

Fig. 4. Effect of temperature on copper dissolution from chalcopyrite.

temperature increments can notably enhance reaction and leaching rates. In aforementioned case, the chemical reaction step might not control the process as there is only a small improvement in copper dissolution rates with a 10 °C temperature increase [40].

Exploring various leaching outcomes reveals a complex relationship between temperature and copper leaching rates from chalcopyrite (Fig. 4). While some studies suggest that higher temperatures enhance the leaching rate in a glycine system, others report a negative correlation [36,41,42]. Khezri *et al.* (2020) [43] identified a threshold where further temperature increases actually reduce copper dissolution. This negative interaction could stem from different scenarios. One possibility is that impurities present during copper leaching from chalcopyrite might influence the outcome. Moreover, glycine can decompose at high temperatures, leading to less available glycinate in solution and reduced copper dissolution. This suggests a need for further research to investigate how temperature affects the chalcopyrite dissolution rate in the presence of different impurities, considering the probable formation of some precipitates.

(2) Effect of initial glycine concentration.

The copper dissolution rate rose with increased initial glycine concentrations (Fig. 5) [40,42,51]. Beyond a certain level, adding further glycine at the initial stage of the process failed to further boost copper dissolution [40]. Studies show that copper extraction increased from 13% to 14% when glycine concentrations rose from 0.5 to 2 M over 96 h. However, experiments were mostly conducted at ambient temperature, using fresh solutions and oxidants. Maintaining a constant glycine concentration of 1.0 M while periodically regenerating it during experiments resulted in copper leaching increasing from 14% to 21% at room temperature after 96 h. By charging lixiviant (glycine) and oxidant (hydrogen peroxide) every 24 h, copper extraction soared to 42% after 168 h [41]. It should be noted that varying raw materials can lead to different trends in copper dissolution percentages.

Table 2
Effect of particle size on copper dissolution from malachite (leaching time: 3 h) and chalcocite (leaching time: 48 h) [40,51].

Size fraction (μm)	Copper extraction (%)	
	Malachite	Chalcocite
+75–106	82.8	31.0
+53–75	89.5	31.0
+38–53	99.0	43.0
+20–38	99.9	43.0
P_{100}-20	—	78.2

Note: P_{100}-20: 100% of particles < 20 μm.

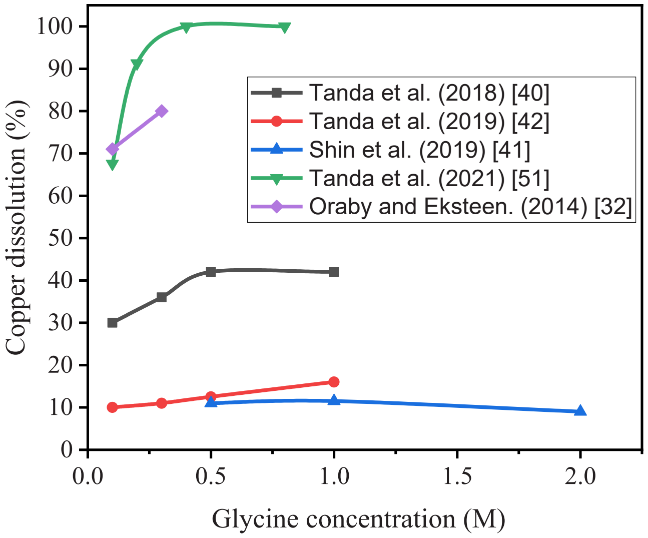

Fig. 5. Effect of glycine concentration on copper dissolution.

(3) Effect of particle size.

The particle size and type are crucial factors in kinetic modeling using the shrinking core model. When the dissolution rate is mainly associated with particle size, it indicates that diffusion through the product layer is likely the controlling kinetic mechanism [40,42,51]. Understanding interactions between particle size and glycine in copper leaching kinetics can help identify the controlling steps for different minerals. Studies on copper leaching kinetics from chalcocite and malachite (Table 2) show that copper extraction generally increases as particle size decreases. This indicates that diffusion through the product layer may be the controlling step in both processes. However, in the malachite leaching process, reducing particle size below a specific threshold (−53 μm) results in negligible improvements in copper extraction rates. Thus, the chemical reaction step largely controls malachite leaching below a special particle size, while diffusion phenomena and mineralogical factors like crystal structure and mineral composition play critical roles in the process [40,51].

According to another investigation, the influence of particle size on copper leaching rates from fine chalcopyrite for particles sized −20 μm showed (Fig. 6) that there was no remarkable difference in copper

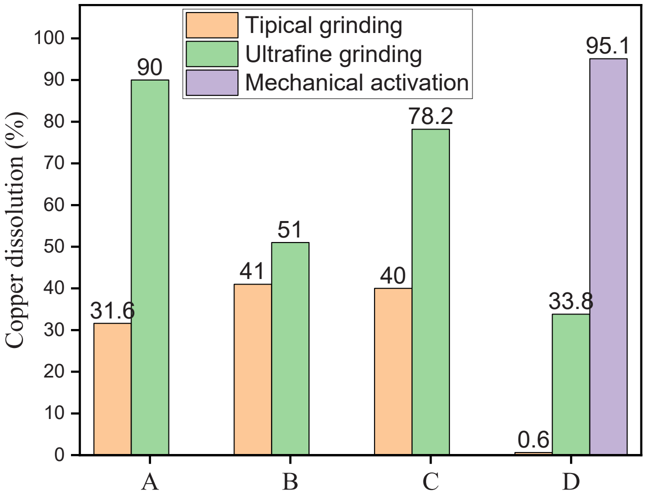

Fig. 6. Effect of ultrafine grinding on copper leaching from (A) chalcopyrite specimen [42], (B) chalcopyrite concentrate [43], (C) chalcocite specimen [40], and (D) chalcopyrite specimen [44].

extraction when comparing size fractions of +38–53 to +20–38 μm, both achieving around 32.0% after 96 h. Surprisingly, the P_{100}-10 μm (100% of particles < 10 μm) fraction achieved about 90% copper extraction, with a notable 46.8% extraction within the first 6 h, which was significantly higher than the 1.7% copper dissolution observed in other size fractions during the same timeframe [42]. The remarkable improvement in copper extraction below the P_{100}-10 μm fraction is likely attributed to mechanochemical activation of chalcopyrite during grinding. The ultrafine specimen of A, in comparison with the ultrafine specimen of D, shows a significantly higher dissolution rate that can be routed in the different leaching conditions of the two studies. One study featured a blend with 10wt% pyrite, and the experiment ran for 96 h, while another used museum-grade chalcopyrite without pyrite for only 12 h [44,45].

(4) Effect of stirring speed.

Research has shown that increasing the stirring speed up to a certain point enhances copper dissolution from chalcocite. However, beyond the optimum speed, copper extraction rates decline. This decrease is likely attributed to reduced contact between particles and the oxidant at high striping speeds. The result of chalcocite leaching kinetic rates indicated that by increasing the stirring speed from 200 to 800 r/min (200, 400, 600, and 800 r/min), copper extraction enhanced up to a special point (52.4%) with a stirring speed of 600 r/min but decreased to 44.1% with a stirring speed of 800 r/min [40]. By contrast, according to studies on chalcopyrite leaching kinetics, increasing the stirring speed from 200 to 800 r/min resulted in copper dissolution increasing from 25% to 39%, with a constant initial glycine concentration of 0.5 M [42]. Regarding malachite, copper dissolution improved as the stirring speed increased from 150 to 350 r/min. However, no further gains were observed when the speed increased to 550 and 800 r/min compared to 350 r/min [51].

(5) Effect of dissolved oxygen (DO).

Investigating the effect of dissolved oxygen concentration on copper leaching from chalcopyrite and chalcocite using glycine reveals that an increase in copper concentration generally boots the copper dissolution rates, mostly in the early stages of the process [42]. However, experimental results indicate that beyond a certain point, further increases in dissolved oxygen concentration do not enhance copper extraction. The main reasons accounting for this phenomenon are unclear but mainly involve glycine degradation when exposed to prolonged oxidant interaction. Moreover, it could be rooted in the formation of copper alteration products on the mineral surfaces under high dissolved oxygen concentrations [40].

2.2. Glutamic acid/glutamate

2.2.1. Background

Glutamic acid, a nonvolatile reagent, is essential for protein synthesis and is the most prevalent excitatory neurotransmitter in the central nervous system. It is widely used as a food condiment owing to its low cost and safety at low concentrations [52].

2.2.2. Application of glutamic acid in copper leaching

Recent research has explored the potential of glutamic acid ($C_5H_9NO_4$) as a solvent for copper dissolution. Monosodium glutamate in alkaline solutions has been used to leach copper from waste electrical and electronic equipment (WEEE). Studies examined the impact of oxidizing agents such as hydrogen peroxide (H_2O_2) and potassium permanganate ($KMnO_4$) on copper leaching efficiency using glutamic acid, comparing it with glycine. Results showed 92% copper recovery in 2 h using 0.03 M H_2O_2 and 0.5 M monosodium glutamate at pH 9.44 at room temperature, outperforming glycine, which achieved 85% recovery [19]. Despite its promise as a copper solvent, glycine remains advantageous owing to its low cost, low molecular weight, and industrial availability [13].

Moreover, glutamic acid could selectively extract approximately 99% zinc and 86% copper from furnace dust using 1 M monosodium glutamate and 5% solids at pH 9 [18]. A comparison between the performance of glutamic acid (10 g/L, initial pH 7) and *Bacillus* strains of heterotrophic bacteria for copper leaching from complex ores indicated that glutamic acid exhibited superior performance, achieving a copper leaching rate of 43.6% compared to 24%–29% achieved by bacterial strains over 28 d [17].

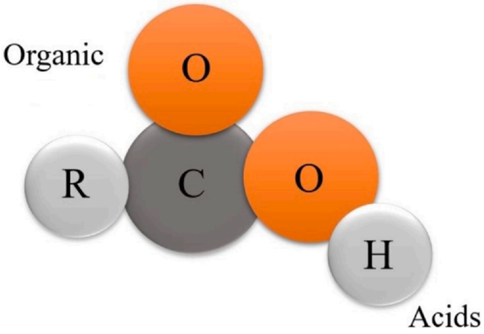

Fig. 7. Schematic structure of organic acids [53].

In general, these limited studies highlighted glutamic acid's potential as a solvent for copper leaching. The results indicate promising extraction rates, especially when combined with oxidizing agents or used selectively for impurity removal. Further research is essential to fully understand and optimize glutamic acid's role in copper leaching processes from various copper minerals and ores.

3. Organic acids

Organic acids, found naturally in animals, plants, and microorganisms, are produced by fungi, yeasts, and bacteria. Classified as "weak" acids, they do not completely dissolve in water and consist of one or more carboxylic acid groups covalently linked in compounds such as amides, esters, and peptides (Fig. 7).

Similarly to inorganic acids, organic acids have a pH value below 7, a sour taste, and release hydrogen ions when dissolved in water. They are corrosive to human tissue and react with bases to form salts and water [54]. Recently, organic acids have gained attention as "eco-friendly" lixiviants for dissolving metals, particularly copper, offering a promising alternative to toxic leaching agents. Their ability to form complexes with copper ions enhances copper dissolution, while their natural occurrence makes them appealing for sustainable metal extraction [55]. However, further research and optimization are needed to fully understand their potential and limitations in industrial applications. The organic acids that have been extensively studied for this purpose include citric acid, formic acid, acetic acid, and oxalic acid (Table 3).

3.1. Citric acid

Citric acid ($C_6H_8O_7$, CA), commonly found in fruits and vegetables, is a weak organic acid often used in food. It has also proven effective as a leaching agent for dissolving copper by forming complexes with copper ions (Eq. (5)) as a weak acid, facilitating their dissolution in water [61]. When comparing the copper extraction efficiency from CuO/Al_2O_3 catalysts using different solutions in a batch reactor, it was found that inorganic acids, H_2SO_4, HCl, HNO_3, and CA dissolved 99.95% of copper after 14 min at 0.5 M and 25 °C. By contrast, CA required 2 h at 80 °C to achieve the same level of dissolution efficiency. Hydrochloric acid yielded the highest CuO dissolution efficiency. However, CA is considered technically feasible for copper leaching from various minerals such as malachite (Eq. (6)) [61].

$$3CuO + 2C_6H_8O_7 \rightarrow Cu_3(C_6H_5O_7)_2 + 3H_2O \tag{5}$$

$$Cu(OH)_2 \cdot CuCO_3 + 2C_6H_8O_7 \rightarrow 2Cu^{2+} + 2C_6H_6O_7 + CO_2 + 3H_2O \tag{6}$$

Table 3
Dissolution of different copper minerals using various organic acids.

Sample	Reagent	Organic acid concentration	Particle size	Oxidant	Pulp density	pH	Temperature (°C)	Leaching time (h)	Stirring speed (r/min)	Recovery	Ref.
Malachite	Citric acid	0.2 M	105 − 150 µm	—	5wt%	10.5	40	0.5	200	91.61%	[56]
Malachite	Formic acid	0.4 M	+75 − 30 µm	—	10 mL/g	—	Ambient	1.5	200	70.25%	[57]
Chalcopyrite	Oxalic acid	100 g/L	$d_{90^*} = 56$ µm	3 M H_2O_2	25 mL/g	—	170	3	400	88.5%	[58]
Slag	Citric acid	2 N	90% < 45 µm	—	10wt%	2.1	Ambient	8 − 9	—	4.47%	[59]
Soil	Citric acid	0.1 M	> 2 mm	—	—	5	Ambient	24 h batch leaching and 20 d column leaching	—	14.2% Cu with batch leaching and 11.1% column leaching	[60]
Catalyst with 10% CuO	Citric acid	0.5 M	80 µm	—	40 mL/g	1.6	80	2	400	99.95%	[61]
WPCB	Citric acid	0.5 M	> 500 µm	0.1 M H_2O_2 additions per hour	20 g/L	4.5	30	5	125	86%	[62]
WPCB	Citric acid + Acetic acid	1 M citric acid, 5vol % acetic acid	3 cm × 3 cm	5% H_2O_2	2.5 g/L	—	Ambient	24	—	325.89 ppm	[63]
WPCB	Oxalic acid	50 mM	0.01 − 150 µm	—	0.3 g/80 mL	5.1	Moderate	42 d	—	13% Cu, 7% Pb, 2% Zn, 39% Cd	[64]
E-waste	Citric acid	50 mM	0.01 − 150 µm	—	0.3 g/80 mL	5.1	Moderate	42 d	—	67% Cu, 91% Pb, 92% Zn, 71% Cd	[64]

Notes: WPCB—Waste-printed circuit boards. d_{90} refers to the 90% passing size. N (normality) is the gram equivalent weight of solute per liter of solution.

By optimizing various parameters, including particle size (+105–150 µm), acid concentration (0.2 M), and solid-to-liquid ratio (1:20 g/mL) at 40 °C after 30 min, 91.61% of copper can be extracted from an oxidized copper ore containing malachite. Increasing temperature did not significantly affect copper extraction [56].

Moreover, CA was examined for its ability to selectively dissolve lead over copper from flash smelting slag [65]. The results show that copper dissolution remained mainly under 35% without additives, short leaching times, and ambient temperature. Under optimal conditions for lead leaching with CA (1 mol/dm^3 of citric acid, 30 min, 70 °C, and liquid-to-solid ratio = 5), copper leaching remained less than 10% [65]. CA also facilitated selective extraction of base metals from copper granulated slag (0.53wt% Cu) at atmospheric conditions, recovering 4.47% copper, 88.3% cobalt, 95% nickel, and 93.8% iron in the first leaching stage using 2 N CA at room temperature and 10% pulp density (weight/volume) over 8–9 h. However, CA alone could not fully recover copper, which remained in its elemental state even after prolonged leaching [59]. Ke *et al.* (2020) [60] examined CA to reduce heavy metal concentrations, such as cadmium, lead, copper, and zinc, in smelter soil using batch and column leaching processes. They found that CA concentration and pH significantly affected the effectiveness of heavy metal removal during batch leaching. The pH also influenced the chelation of heavy metals by altering the existing form of CA in the solution. The maximum efficiency for removing heavy metals through batch leaching was achieved at a concentration of 0.1 M and a pH of 5, resulting in the extraction of 89.1% cadmium, 26.8% lead, 41.7% zinc, and 14.2% copper. CA also removed significant amounts of heavy metals (91.3% cadmium, 11.1% lead, 39.2% zinc, and 11.1% copper) through column leaching. The lower copper dissolution with CA leaching compared to other studies, like those by Habbache *et al.* (2009) [61] and Shabani *et al.* (2012) [56], can be attributed to differences in copper resources, leaching conditions such as the concentration of other heavy metals, the copper form, redox potential, leach liquor pH, and the absence of oxidizing agents like H_2O_2.

3.1.1. Role of auxiliary oxidants

CA has also been used to extract copper from waste printed circuit boards, though the dissolution rate was slow. To enhance copper extraction, adding auxiliary oxidants like H_2O_2 or accelerators like acetic acid is necessary [62–64]. Despite the slow rate, the CA leaching process with H_2O_2 is more ecofriendly, stable, and safer compared to HCl leaching. Using 0.1 M H_2O_2 per hour over a 5-h leaching process resulted in 93% copper dissolution under conditions of 0.5 M sodium citrate, pH 4.5, and a solid-to-liquid ratio of 2:100 [66].

3.1.2. Role of temperature

The temperature played a crucial role in the leaching kinetics of copper, lead, and iron from gravity-concentrated waste printed circuit boards in citrate acid–peroxide media, which had a metallic content exceeding 90wt% [62]. Under optimal conditions, pH 4.5, a solid-to-liquid ratio of 2:100, and 0.5 M sodium citrate, temperature variations from zero to 70 °C significantly influenced copper, lead, and iron leaching kinetics. Increasing the temperature to 30 °C enhanced metal dissolution, aligning with kinetic theory. Although the highest initial leaching rates occurred at 70 °C within the first hour, overall metal dissolution declined after this period. In fact, the highest copper dissolution rates after 5 h were obtained at 30 °C. This is likely attributed to citrate degradation, suggesting a need for further investigation into the mechanisms of citrate transformation and degradation to improve the viability of this process.

3.2. Oxalic acid

Oxalic acid ($C_2H_2O_4$, OA) is a dicarboxylic acid that is found in various plants, such as rhubarb and spinach. It can also be synthesized from ethylene glycol or glycerol. It dissolves copper by effectively forming soluble copper oxalate complexes and can be used with H_2O_2 in a pressure reactor system to extract copper from chalcopyrite concentrate [58]. Results obtained from studies showed that copper and iron, when combined with OA, have different dissolution coefficients, allowing selective metal extraction based on temperature. For instance, 90.6% of iron and 1.73% of copper were extracted after 3 h of leaching at 45 °C with 5 M H_2O_2 and 100 g/L $C_2H_2O_4$. Conversely, at 170 °C with 3 M H_2O_2 and the same concentration of OA, 88.5% copper and 2.11% iron were extracted. This shows selective leaching can be achieved by increasing temperature, as copper and iron oxalates dissolve differently in the presence of OA. During the autoclave leaching process with H_2O_2, the dissolution behaviors of copper and iron change, reversing at a certain temperature. At lower temperatures, copper remains in solid form as oxalate, while iron dissolves into the solution. However, as the temperature increases, this behavior reverses; that is, iron becomes solid as hematite, and copper dissolves into the solution as sulfate [58].

Kolenčík *et al.* (2013) [64] performed experiments to evaluate the microbial leaching of heavy metals using *Aspergillus niger (AN)* as a filamentous fungus, compared to traditional acidic methods with OA and CA. According to the data in Table 4, under ambient conditions, OA is found to be the least effective at dissolving heavy metals, including copper, lead, and zinc, compared to the other methods tested.

3.3. Formic acid

Formic acid (HCOOH, FA) is an organic acid naturally produced by some insects and synthesized from carbon monoxide that has shown acceptable efficiency for copper leaching. It has a strong affinity for copper ions and can effectively solubilize them. Yaras and Arslanoglu (2018) [57] investigated the kinetics of copper leaching from malachite ore using FA, exploring the effects of various parameters, including particle size, acid concentration, leaching time, formic acid-to-malachite ratio, reaction temperature, and stirring speed. The optimal conditions they identified included a particle size of +75–30 µm, FA concentration of 0.4 mol/L, leaching time of 90 min, FA (volume)/malachite (weight) ratio of 10 mL/g, and a temperature of 25 °C, achieving a copper extraction rate of 70.25%. Kinetic modeling was used to evaluate how these parameters affect the copper leaching process and highlighted that the controlling mechanism for copper leaching from malachite in an FA solution is primarily governed by film diffusion through a product layer.

3.4. Acetic acid

Acetic acid (CH_3COOH, AA), commonly known as vinegar, is a weak acid that can be produced from the oxidation of grain alcohol or through the fermentation of fruit sugar in cider. It demonstrates copper-dissolving properties and can form complexes with copper ions. Research into the kinetics of copper leaching from malachite ore using AA shows that the leaching rate increases with higher AA concentration, faster stirring speed, raised temperature, smaller particle size, and a lower solid-to-liquid ratio. The leaching reaction aligns with a mixed kinetic control model accounting for diffusion through the product layer at temperatures between 20 and 45 °C and a surface chemical reaction between 45 and 60 °C. The activation energies for these consecutive steps are 26.45 and 80.15 kJ/mol, respectively [67].

Table 4
The efficiency (%) of leached heavy metals by *Aspergillus niger* and long chemical leaching with 0.05 M citric acids and 0.5 M oxalic acids from electronic scrap after 42 d [64].

Metal	*AN*	Oxalic acid	Citric acid
Cu	68.27	13.28	67.45
Pb	27.92	7.43	91.42
Zn	4.08	1.82	91.99
Cd	21.90	38.92	70.80

3.5. Mixed leaching agents

Research has shown that using a mixture of organic acids can enhance the copper leaching process, exhibiting synergistic effects. A mixture of CA, AA, and H_2O_2 has been used to boost copper leaching efficiency from waste printed circuit boards. This study examined the influence of systemic factors such as the ratios of organic acids, their concentrations, and H_2O_2 concentration on copper leaching. The results show that this mixture significantly improves copper leaching efficiency, with the highest copper dissolution (325.89 ppm) achieved using a leaching solution containing 1 M CA, 5% AA, and 5% H_2O_2. These findings indicate that this combination could serve as a standardized method for copper leaching from waste printed circuit boards and suggest that these organic acids can be ecofriendly alternatives to inorganic acids for waste recycling [63].

4. Conclusions

The adoption of ecofriendly leaching agents, particularly amino and organic acids, marks a significant move towards sustainable mining practices and the green transition. The use of these organic acids is crucial, especially when traditional leaching agents like sulfuric acid pose environmental and technical challenges, such as excessive consumption by carbonates, conversion of silicates into gels, and iron impurity dissolution. These environmentally friendly reagents also allow for the selective removal of specific impurities from the ore.

Glycine is recognized as the most effective amino acid for copper leaching, particularly in ores containing impurities and carbonate. Common copper minerals such as azurite, malachite, bornite, and cuprite respond well to glycine leaching. However, chalcopyrite, chrysocolla, and conichalcite are known to be highly refractory with lower reactivity to glycine.

Kinetic studies reveal that copper dissolution with glycine generally increases with higher dissolved oxygen concentration (combined with oxidizing agents), elevated temperatures, increased initial glycine concentration, and smaller mineral particle sizes. However, beyond a certain point, additional glycine concentration does not significantly enhance copper dissolution at the onset of the process. Temperature plays a crucial role in enhancing copper leaching efficiency although the relationship between temperature and the leaching rate of copper from chalcopyrite can be complex due to factors such as glycine decomposition, conversion, and reduced oxygen concentration in the solution.

Organic acids such as citric, formic, acetic, and oxalic acids are extensively studied for copper leaching. The effectiveness of these acids varies depending on the copper resource and specific leaching conditions. Citric acid has demonstrated the ability to extract over 90% of copper from malachite at room temperature. High copper dissolution rates from CuO/Al_2O_3 have observed at elevated temperatures. FA has shown effectiveness with a 70.25% extraction rate from malachite ore under optimum conditions, including a particle size of +75–30 µm, FA concentration of 0.4 mol/L, leaching time of 90 min, FA/malachite ratio of 10 mL/g, and a temperature of 25 °C. Kinetic modeling indicates film diffusion through a product layer as the controlling mechanism for copper leaching from malachite in FA.

Controlling temperature is crucial in the selectivity of the copper leaching process using organic acids. At low temperatures (20–45 °C), copper leaching is influenced by a mixed kinetic control model focusing on diffusion through the product layer. At higher temperatures (45–60 °C), the leaching reaction is dominated by surface chemical reactions.

The presence of auxiliary oxidants like H_2O_2 or accelerators in the leaching solution is often necessary to enhance copper extraction, particularly from electronic wastes. Using a combination of organic acids could provide a standardized method for enhancing copper leaching efficiency from waste materials.

5. Future perspectives

In advancing ecofriendly leaching agents for copper extraction, several critical areas demand deeper exploration and innovation. To fully harness the potential of amino and organic acids in sustainable mining practices, it is vital to address these critical aspects.

(1) Reproducibility and Error Analysis: One of the essential factors in hydrometallurgical experiments is the reproducibility of results. Most current studies rely on single experimental runs, leaving room for potential errors and variability in outcomes. Future research should prioritize repeating experiments under consistent conditions to validate the reproducibility of results and provide a more reliable understanding of the leaching processes.
(2) Comprehensive Characterization of Feed and Tail Samples: To optimize the leaching process, a thorough characterization of feed and tail samples is crucial. Future studies should systematically report on mineralogy, the grade of all affecting ions, and the galvanic effects of sulfidic minerals. Advanced analytical techniques such as XRD, XRF, and FTIR should be employed to monitor the solid composition and assess the degradation of glycine and other reagents, particularly at elevated temperatures.
(3) Kinetics and Mechanism Studies: While many studies have focused on achieving high copper recovery rates, the fundamental kinetics and mechanisms of copper leaching in amino and organic acid media are not fully understood. Detailed kinetic modeling and mechanistic studies are essential to unravel the interactions between different variables and their impacts on leaching efficiency. This knowledge will be crucial for optimizing the leaching process and improving copper extraction selectivity.
(4) Exploration of Diverse Organic Acids: The research on organic acids for copper leaching has primarily concentrated on a limited number of acids such as citric, formic, acetic, and oxalic. However, there is a need to explore other organic acids that may offer unique benefits in selectivity, biodegradability, and environmental impact. Testing a broader range of organic acids could uncover new possibilities for copper extraction from both primary and secondary resources.
(5) Pilot and Industrial-scale Investigations: Current studies are mostly limited to the laboratory scale, which limits the understanding of the economic feasibility and scalability. Future research should focus on scaling up to pilot and industrial levels to evaluate economic aspects, energy consumption, and potential challenges associated with large-scale implementation. Such studies are crucial for assessing the viability of using amino and organic acids in commercial mining operations.
(6) Life Cycle Assessment and Environmental Impact: Conducting a comprehensive life cycle assessment (LCA) is essential to quantify the environmental benefits and potential trade-offs of using amino and organic acids in copper leaching. Future studies should encompass the entire process, from reagent production to waste management, ensuring that these ecofriendly methods genuinely advance sustainable mining. Incorporating LCA into the evaluation process will pinpoint improvement areas and guide the development of more sustainable practices.
(7) Monitoring and Automation of Key Process Parameters: Precise control over key process parameters such as pH, temperature, and reagent concentration is essential for optimizing leaching performance and ensuring consistent product quality. Future studies should incorporate advanced sensing technologies and automation systems to enable real-time monitoring and adjustments of operating conditions. This approach will enhance efficiency and reliability in copper leaching processes, particularly in complex and variable ore environments.
(8) Equipment Innovation and Optimization: Successfully applying green reagents in copper leaching requires the development of specialized reactors, materials, and monitoring systems. Future research should focus on designing and optimizing equipment tailored to the challenges associated with amino and organic acids, such as reagent stability, temperature control, and reaction kinetics. Innovations in equipment design will be pivotal in achieving greener and more efficient copper leaching operations.

By addressing these critical areas in future studies, the full potential of ecofriendly leaching agents for copper extraction can be realized, paving the way for sustainable and environmentally responsible mining practices.

CRediT authorship contribution statement

Hassan Safari: Conceptualization, Data curation, Writing – original draft. **Mohammad Rezaee:** Conceptualization, Data curation, Writing – original draft. **Saeed Chehreh Chelgani:** Writing – review & editing.

Declaration of Competing Interest

Saeed Chehreh Chelgani is an editorial board member for this journal and was not involved in the editorial review or the decision to publish this article. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] International Copper Study Group (ICSG), Copper: Preliminary Data for September 2020, ICSG, Lisbon, Portugal, 2020.
[2] J. Doebrich, Copper—A metal for the ages, U.S. Geological Survey, 2009.
[3] K.C. Misra, Understanding Mineral Deposits, Springer, Dordrecht, 2012.
[4] M.E. Schlesinger, K.C. Sole, W.G. Davenport, G.R.A. Flores, Extractive Metallurgy of Copper, Elsevier, 2021.
[5] Z.H. Ren, P. Krishnamoorthy, P.Z. Sanchez, E. Asselin, D.G. Dixon, N. Mora, Catalytic effect of ethylene thiourea on the leaching of chalcopyrite, Hydrometallurgy 196 (2020) 105410.
[6] S.H. Yin, L.M. Wang, A.X. Wu, X. Chen, R.F. Yan, Research progress in enhanced bioleaching of copper sulfides under the intervention of microbial communities, Int. J. Miner. Metall. Mater. 26 (11) (2019) 1337–1350.
[7] R.P. Hackl, D.B. Dreisinger, E. Peters, J.A. King, Passivation of chalcopyrite during oxidative leaching in sulfate media, Hydrometallurgy 39 (1–3) (1995) 25–48.
[8] B.C. Tanda, J.J. Eksteen, E.A. Oraby, An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions, Hydrometallurgy 167 (2017) 153–162.
[9] Statista, Refined copper usage worldwide from 2010 to 2022, Statista, 2023. ⟨https://www.statista.com/statistics/267849/global-copper-consumption/⟩ (Accessed September 2023).
[10] International World Copper Council (IWCC), Major End Uses of Copper Worldwide Report, IWCC, 2023.
[11] E. Ebrahimi, H. Safari, M. Rezaee, A. Rezaei, H. Abdollahi, An environmentally friendly method for extraction of cobalt and molybdenum from spent catalysts using deep eutectic solvents (DESs), Environ. Sci. Pollut. Res. Int. 30 (39) (2023) 90243–90255.
[12] D. Feng, J.S.J. van Deventer, The role of amino acids in the thiosulphate leaching of gold, Miner. Eng. 24 (9) (2011) 1022–1024.
[13] H. Li, Z.X. Deng, E. Oraby, J. Eksteen, Amino acids as lixiviants for metals extraction from natural and secondary resources with emphasis on glycine: a literature review, Hydrometallurgy 216 (2023) 106008.
[14] H. Li, E. Oraby, J. Eksteen, Extraction of copper and the co-leaching behaviour of other metals from waste printed circuit boards using alkaline glycine solutions, Resour. Conserv. Recycl. 154 (2020) 104624.
[15] M. Rezaee, R. Saneie, A. Mohammadzadeh, H. Abdollahi, M. Kordloo, A. Rezaee, E. Vahidi, Eco-friendly recovery of base and precious metals from waste printed circuit boards by step-wise glycine leaching: process optimization, kinetics modeling, and comparative life cycle assessment, J. Clean. Prod. 389 (2023) 136016.
[16] I. Jamett, P. Carrasco, M. Olmos, P. Hernández, Glycine/glutamate: "green" alternatives to recover metals from minerals/residues—Review of current research, Minerals 13 (1) (2022) 22.
[17] S. Kostudis, K. Bachmann, S. Kutschke, K. Pollmann, J. Gutzmer, Leaching of copper from Kupferschiefer by glutamic acid and heterotrophic bacteria, Miner. Eng. 75 (2015) 38–44.
[18] E. Prasetyo, C. Anderson, F. Nurjaman, M. Al Muttaqii, A.S. Handoko, F. Bahfie, F.R. Mufakhir, Monosodium glutamate as selective lixiviant for alkaline leaching of zinc and copper from electric arc furnace dust, Metals 10 (5) (2020) 644.
[19] C.G. Perea, O.J.R. Baena, C.F. Ihle, H. Estay, Copper leaching from wastes electrical and electronic equipment (WEEE) using alkaline monosodium glutamate: thermodynamics and dissolution tests, Clean. Eng. Technol. 5 (2021) 100312.
[20] B. Musariri, G. Akdogan, C. Dorfling, S. Bradshaw, Evaluating organic acids as alternative leaching reagents for metal recovery from lithium ion batteries, Miner. Eng. 137 (2019) 108–117.

[21] M.A. Razak, P.S. Begum, B. Viswanath, S. Rajagopal, Multifarious beneficial effect of nonessential amino acid, glycine: a review, Oxid. Med. Cell Longev. 2017 (2017) 1716701.

[22] D.M. Muir, A review of the selective leaching of gold from oxidised copper–gold ores with ammonia–cyanide and new insights for plant control and operation, Miner. Eng. 24 (6) (2011) 576–582.

[23] H. Mokhlis, R. Drissi Daoudi, M. Azzi, Study of the electrochemical behavior of printed circuit boards (PCBs) leaching solutions using glycine and copper recovery by electrodeposition from leachate solutions, Mater. Today Proc. 37 (2021) 3973–3979.

[24] M. Rezaee, S.Z. Shafaei, H. Abdollahi, S. Mohammadnejad, A. Mabudi, An experimental and DFT study on using the thiosulfate–glycine complex as an alternative agent of cyanide in the gold leaching process, J. Sustain. Metall. 9 (3) (2023) 1239–1252.

[25] M. Sarvar, Z. Shafaei Tonkaboni, M. Noaparast, A.R. Badiei, A. Amiri, Application of amino acids for gold leaching: effective parameters and the role of amino acid structure, J. Clean. Prod. 391 (2023) 136123.

[26] G.C. Barrett, Chemistry and Biochemistry of the Amino Acids, Springer, Dordrecht, 2012.

[27] F. Faraji, J.X. Wang, H. Mahandra, A. Ghahreman, A green and sustainable process for the recovery of gold from low-grade sources using biogenic cyanide generated by *Bacillus megaterium*: a comprehensive study, ACS Sustain. Chem. Eng. 9 (1) (2021) 236–245.

[28] F. Wissing, Cyanide formation from oxidation of glycine of Pseudomonas species, J. Bacteriol. 117 (3) (1974) 1289–1294.

[29] Global Sources, 2021. 〈https://www.globalsources.com/?utm_source=1907412&source=1907412&gad_source=1&gclid=CjwKCAjw_4S3BhAAEiwA_64YhuTFGejsBUTYt_iuycYAfs0DLC20toLWcHtrIKE7jBXhGRPDIUpdvxoC2BIQAvD_BwE〉.

[30] B.C. Tanda, Glycine as a Lixiviant for the Leaching of Low Grade Copper–gold Ores (Dissertation), Curtin University, Perth, Australia, 2017.

[31] F.H. Al-Jeboori, T.A. Mussa Al-Shimiesawi, O.M. Noori Jassim, Synthesis and characterization of some essential amino acid metal complexes having biological activity, J. Chem. Pharm. Res. 5 (10) (2013) 172–176.

[32] E.A. Oraby, J.J. Eksteen, The selective leaching of copper from a gold–copper concentrate in glycine solutions, Hydrometallurgy 150 (2014) 14–19.

[33] E.A. Oraby, J.J. Eksteen, B.C. Tanda, Gold and copper leaching from gold–copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide, Hydrometallurgy 169 (2017) 339–345.

[34] M. Battur, Geometallurgical Study of Copper Whole Ore from an Open Pit Mine with Various Leaching Systems (Dissertation), University of Arizona, Tucson, USA, 2021.

[35] S. Aksu, F.M. Doyle, Electrochemistry of copper in aqueous glycine solutions, J. Electrochem. Soc. 148 (1) (2001) B51–B57.

[36] J.J. Eksteen, E.A. Oraby, B.C. Tanda, A conceptual process for copper extraction from chalcopyrite in alkaline glycinate solutions, Miner. Eng. 108 (2017) 53–66.

[37] G.M. O'Connor, K. Lepkova, J.J. Eksteen, E.A. Oraby, Electrochemical behaviour of copper in alkaline glycine solutions, Hydrometallurgy 181 (2018) 221–229.

[38] I. Barton, J. Ahn, J. Lee, Mineralogical and metallurgical study of supergene ores of the Mike CuAu(Zn) deposit, Carlin trend, Nevada, Hydrometallurgy 176 (2018) 176–191.

[39] J. Ahn, I.F. Barton, D. Shin, J. Lee, The study of copper leaching from conichalcite and chalcopyrite using alternative lixiviants, in: G. Lambotte, J. Lee, A. Allanore, S. Wagstaff (Eds.), Materials Processing Fundamentals 2018. TMS 2018. The Minerals, Metals & Materials Series, Springer, Cham, 2018, pp. 171–180.

[40] B.C. Tanda, J.J. Eksteen, E.A. Oraby, Kinetics of chalcocite leaching in oxygenated alkaline glycine solutions, Hydrometallurgy 178 (2018) 264–273.

[41] D. Shin, J. Ahn, J. Lee, Kinetic study of copper leaching from chalcopyrite concentrate in alkaline glycine solution, Hydrometallurgy 183 (2019) 71–78.

[42] B.C. Tanda, J.J. Eksteen, E.A. Oraby, G.M. O'Connor, The kinetics of chalcopyrite leaching in alkaline glycine/glycinate solutions, Miner. Eng. 135 (2019) 118–128.

[43] M. Khezri, B. Rezai, A. Akbar Abdollahzadeh, M. Molaeinasab, B.P. Wilson, M. Lundström, Glycine leaching of Sarcheshmeh chalcopyrite concentrate at high pulp densities in a stirred tank reactor, Miner. Eng. 157 (2020) 106555.

[44] M. Khezri, B. Rezai, A.A. Abdollahzadeh, B.P. Wilson, M. Molaeinasab, M. Lundström, Investigation into the effect of mechanical activation on the leaching of chalcopyrite in a glycine medium, Hydrometallurgy 203 (2021) 105492.

[45] D. Dreisinger, Copper leaching from primary sulfides: options for biological and chemical extraction of copper, Hydrometallurgy 83 (1–4) (2006) 10–20.

[46] S. Dasarathy, R.P. Mookerjee, V. Rackayova, V. Rangroo Thrane, B. Vairappan, P. Ott, C.F. Rose, Ammonia toxicity: from head to toe? Metab. Brain Dis. 32 (2) (2017) 529–538.

[47] M. Allameh, M.R. Hosseini, E. Azimi, Development of a sustainable alternative for the ammoniacal cyanidation of copper–gold ores through a biological approach, J. Sustain. Metall. 6 (4) (2020) 796–808.

[48] D. Medina, C.G. Anderson, A review of the cyanidation treatment of copper–gold ores and concentrates, Metals 10 (7) (2020) 897.

[49] E.Y. Yazici, F. Ahlatci, E. Koc, O. Celep, H. Deveci, Pre-treatment of a copper-rich gold ore for elimination of copper interference, in: 8th European Metallurgical Conference, Düsseldorf, 2015, pp. 601–613.

[50] E.A. Oraby, J.J. Eksteen, Gold leaching in cyanide-starved copper solutions in the presence of glycine, Hydrometallurgy 156 (2015) 81–88.

[51] B.C. Tanda, E.A. Oraby, J.J. Eksteen, Kinetics of malachite leaching in alkaline glycine solutions, Miner. Process. Extr. Metall. 130 (1) (2021) 16–24.

[52] L. Sohbatzadeh, S. Shafaei Tonkaboni, M. Noaparast, A. Entezari-Zarandi, A comparative study of malonic and l-glutamic acids for metal leaching from spent lithium-ion batteries: Kinetic and optimization analysis, Minerals 13 (8) (2023) 1104.

[53] P. Meshram, A. Mishra, Abhilash, R. Sahu, Environmental impact of spent lithium ion batteries and green recycling perspectives by organic acids—a review, Chemosphere 242 (2020) 125291.

[54] S. Doores, Organic acids, Food Sci. Technol. N. Y. -Marcel Dekker 145 (2005) 91.

[55] D. Das, S. Mukherjee, M.G. Chaudhuri, Studies on leaching characteristics of electronic waste for metal recovery using inorganic and organic acids and base, Waste Manag. Res. J. Sustain. Circ. Econ. 39 (2) (2021) 242–249.

[56] M.A. Shabani, M. Irannajad, A.R. Azadmehr, Investigation on leaching of malachite by citric acid, Int. J. Miner. Metall. Mater. 19 (9) (2012) 782–786.

[57] A. Yaras, H. Arslanoglu, Leaching behaviour of low-grade copper ore in the presence of organic acid, Can. Metall. Q. 57 (3) (2018) 319–327.

[58] M.D. Turan, Z.A. Sarı, H. Nizamoğlu, Pressure leaching of chalcopyrite with oxalic acid and hydrogen peroxide, J. Taiwan Inst. Chem. Eng. 118 (2021) 112–120.

[59] P. Meshram, L. Bhagat, U. Prakash, B.D. Pandey, Abhilash, Organic acid leaching of base metals from copper granulated slag and evaluation of mechanism, Can. Metall. Q. 56 (2) (2017) 168–178.

[60] X. Ke, F.J. Zhang, Y. Zhou, H.J. Zhang, G.L. Guo, Y. Tian, Removal of Cd, Pb, Zn, Cu in smelter soil by citric acid leaching, Chemosphere 255 (2020) 126690.

[61] N. Habbache, N. Alane, S. Djerad, L. Tifouti, Leaching of copper oxide with different acid solutions, Chem. Eng. J. 152 (2–3) (2009) 503–508.

[62] R. Torres, B. Segura-Bailón, G.T. Lapidus, Effect of temperature on copper, iron and lead leaching from e-waste using citrate solutions, Waste Manag. 71 (2018) 420–425.

[63] N. Nagarajan, P. Panchatcharam, Cost-effective and eco-friendly copper recovery from waste printed circuit boards using organic chemical leaching, Heliyon 9 (3) (2023) e13806.

[64] M. Kolenčík, M. Urík, S. Čerňanský, M. Molnárová, P. Matúš, Leaching of zinc, cadmium, lead and copper from electronic scrap using organic acids and the *Aspergillus niger* strain, Fresenius Environ. Bull. 22 (12a) (2013) 3673–3679.

[65] K. Gargul, B. Boryczko, A. Bukowska, P. Jarosz, S. Małecki, Leaching of lead and copper from flash smelting slag by citric acid, Arch. Civ. Mech. Eng. 19 (3) (2019) 648–656.

[66] R. Torres, G.T. Lapidus, Copper leaching from electronic waste for the improvement of gold recycling, Waste Manag. 57 (2016) 131–139.

[67] M.K. Tanaydın, N. Demirkıran, A. Ekmekyapar, Kinetic model of copper leaching from a malachite ore by acetic acid solutions, J. Chem. Technol. Metall. 55 (2020) 852–859.